Improving the biorefinery output by integrating anaerobic digestion and slow pyrolysis: A case study for cocoa waste

Stef Ghysels[1,2]*, Nayaret Acosta[1,2], Adriana Estrada[1], Mehmet Pala[1], Jo de Vrieze[2], Frederik Ronsse[1] and Korneel Rabaey[2]
[1]*Thermochemical Conversion of Biomass, Ghent University (Belgium)*
[2]*Center for Microbial Ecology and Technology (CMET), Ghent University (Belgium)*
*Stef.Ghysels@UGent.be

Background Agricultural residues hold potential as resources for the recovery of energy, chemicals and materials in a biorefinery, without competing for land-use for primary food and feed production. Cocoa pod husks are an example of a very voluminous agricultural residue, being currently underexploited as bio-refinery feedstock. The annual worldwide production of cocoa beans amounts to 4 million metric tonnes, while cocoa pod husks make out 70-80 wt.% of the cocoa fruit.

This work investigated integrated anaerobic digestion and slow pyrolysis of cocoa pod husks and compared this to the individual processes (Fig. 1). The choice for anaerobic digestion and slow pyrolysis was motivated by (i) the relative low complexity of digestion and slow pyrolysis (relevant for many developing countries), (ii) the generation of additional value from subsequent pyrolysis of digestate, besides biogas from digestion only, and (iii) the hypothesized beneficial lignin-rich nature of the digestate for elevated char yields and liquids rich in interesting phenolic compounds upon slow pyrolysis. The different biorefinery schemes were compared and valued based on the quality and quantity of the biorefinery's output.

Pyrolysis was performed at two temperatures in a fixed-bed reactor, being 350 °C and 500 °C. Comprehensive mass, carbon and energy balances were derived and extensive analysis of the products was performed: biochar (CHNS, heavy metal and pH analysis), pyrolysis liquids (elemental, GC/MS) and non-condensable gases (compact GC).

Results First, it was confirmed that the evolved biogas from anaerobic digestion indeed stemmed from the feedstock's carbohydrates ($CH_{1.7}O_{0.8}$) only, derived from the empirical conversion:
$0.2\ CH_{1.8}O_{0.7}N_{2.3e\text{-}4} + 0.03\ H_2O \rightarrow 0.1\ CH_4 + 0.08\ CO_2$
As the anaerobic digestion process selectively converted the carbohydrate fraction, the digestate indeed was lignin-enriched.

Pyrolysis of this dried digestate at 350 °C (as example) resulted in the mass, carbon and energy balances shown in Fig. 2. This shows an energy/carbon-dense organic liquid phase at a modest mass yield, a high yield in energy/carbon-dense biochar and an energy/carbon-poor aqueous pyrolysis liquid and non-condensable gases. The distribution of mass, carbon and energy was rather similar for pyrolysis at 500 °C, yet a small decrease in biochar mass/energy yield was apparent, in tandem with an increase in the mass/energy yield in non-condensable gases. The biochar's H/C ratio increased while the O/C ratio decreased (*viz.* improved) upon prior digestion of the cocoa pod husks.
Moreover, the increase in the liquid quality was also observed upon prior digestion (Fig. 3). The organic phase contained far less light oxygenates which hold only modest value, while retaining valuable methoxyphenols, methoxyalkyl phenols and alkylphenols, depending on the pyrolysis

temperature. Hence, the organic liquids were more concentrated in valuable compounds for further biorefining.

The overall Sankey diagram of the mass flow in Fig. 4 (carbon and energy not shown here) allows an overall comparative evaluation. It allowed to learn that integrated digestion/pyrolysis could be self-sustaining in terms of energy, by using the energy in the biogas and non-condensable gases. Also, depending on the market situation, biochar yield can be maximized at 350 °C, but its quality in terms of H/C and O/C ratio is better if produced at 500 °C. On the other hand, pyrolysis of digested cocoa at 350 °C resulted in the highest yield in methoxy(alkyl) phenols. Overall, this presentation will outline and compare the various biorefining opportunities and puts forth general guidelines for this particular feedstock, as well as other agricultural residues.

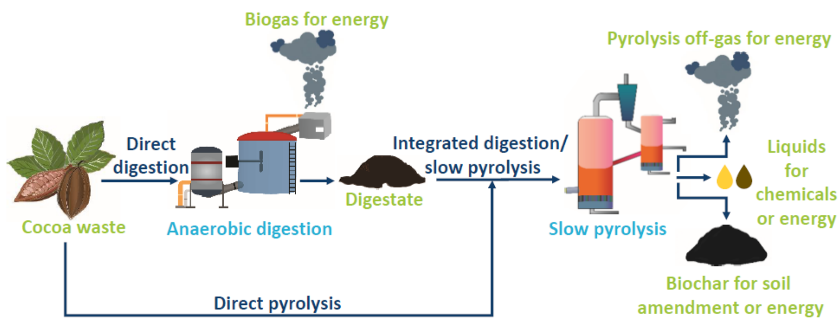

Fig. 1 Overview of the herein studied processes and/or combinations thereof.

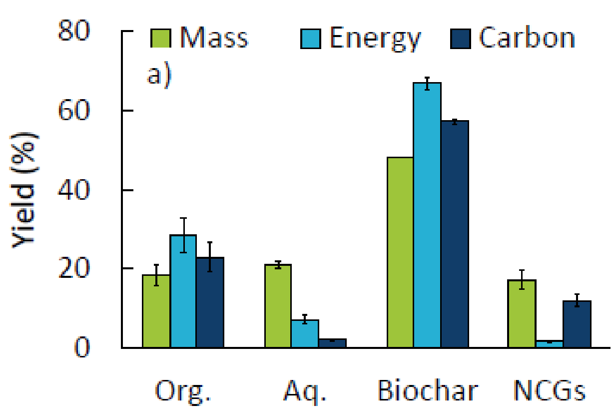

Fig. 2 Mass, energy and carbon balance for pyrolysis products (350 °C) of digested cocoa pod husks.

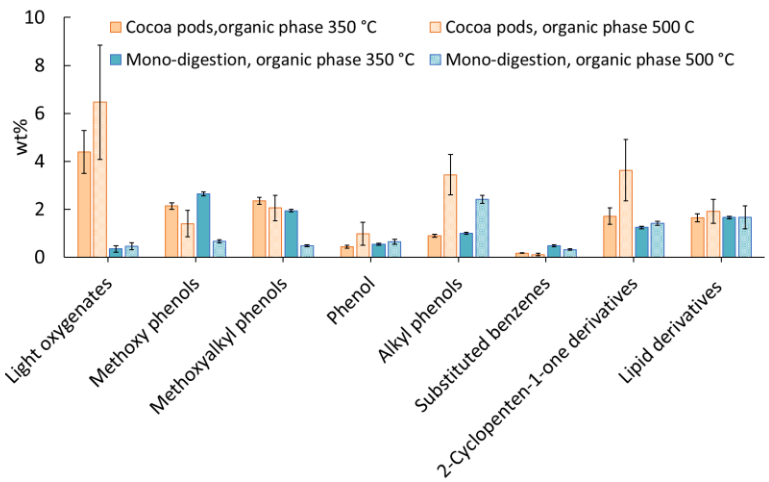

Fig 4. Compositional analysis of organic heavy liquids from slow pyrolysis (350 °C and 500 °C) of undigested cocoa and digested cocoa (denoted as mono-digestion).

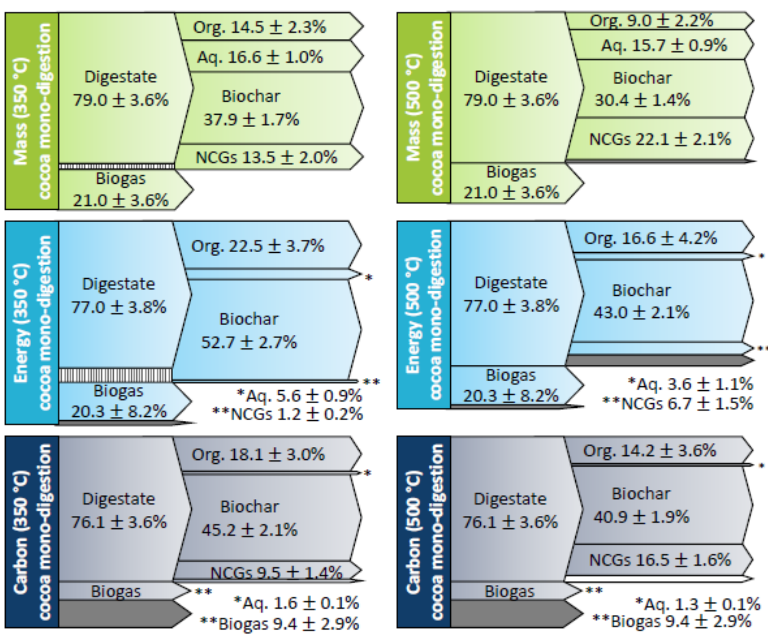

Fig. 5 Sankey diagram for pyrolysis of digested cocoa at 350 °C and 500°C.